

Short Note

3,5-Dimethoxy-2-[(4-methoxyphenyl)diazenyl]phenol

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Abstract: 3,5-Dimethoxy-2-[(4-methoxyphenyl)diazenyl]phenol was synthesized by an azo-coupling reaction between 3,5-dimethoxyphenol and 4-methoxy benzenediazonium tetrafluoroborate. The structure of newly synthesized compound was elucidated based on ¹H NMR, ¹³C NMR, ESI-MS, UV-Vis and FT-IR.

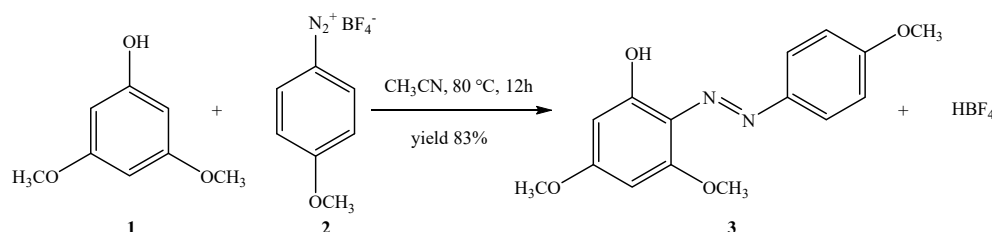
Keywords: benzenediazonium salt; 3,5-dimethoxyphenol; azo-coupling reaction

1. Introduction

Azo compounds are a well-known class of compounds widely used in industry as colorants in textile, cosmetics, and paper-printing fields [1,2]. The principal method for the synthesis of azoic compounds is the azo-coupling reaction, a kind of electrophilic substitution reaction, that is one of the most important and versatile methodologies in organic synthesis [3,4]. From many years, we are studying aromatic substitution reaction, both electrophilic and nucleophilic, including azo-coupling reaction [5–8]. Now we report the synthesis, by azo-coupling reaction, of a novel azo compound, namely 3,5-dimethoxy-2-[(4-methoxyphenyl)diazenyl]phenol.

2. Results

The synthesis of 3,5-dimethoxy-2-[(4-methoxyphenyl)diazenyl]phenol (**3**) (Scheme 1) was performed by reaction between 3,5-dimethoxyphenol (**1**) and 4-methoxy benzenediazonium tetrafluoroborate (**2**) in acetonitrile at 80 °C. The reaction progress was monitored by TLC (R_F of product 0.53 in CH_2Cl_2), and precipitation of a solid was observed. At the end of the reaction, the solid was collected and its ¹H NMR spectrum showed only signals ascribable to compound **3** (52% yield). The TLC analyses of the mother liquor showed the presence of the compound **3**, that was isolated and purified by column chromatography on silica gel using dichloromethane as eluent (31% yield) providing a combined yield of 83%. The structure of newly synthesized compound was elucidated based on FT-IR, UV-Vis, ¹H NMR, ¹³C NMR and ESI-MS spectroscopy (All spectra are reported in supplementary materials).



Scheme 1. Synthesis of compound **3** from 3,5-dimethoxyphenol (**1**) and 4-methoxy benzenediazonium tetrafluoroborate (**2**).

Among the above cited techniques, the most diagnostic were NMR spectroscopy and mass spectrometry. In particular, ^1H NMR spectrum showed different signals for all three methoxy groups and also two separated signals for CH on the phenol ring.

Further, compound **3** showed an interesting solid state fluorescence [9–11] when it was exposed to the UV lamp at 366 nm (Figure 1).



Figure 1. Solid-state fluorescence of compound **3** at 366 nm.

Figures 2 and 3 show the UV-Vis spectrum and emission spectra, respectively.

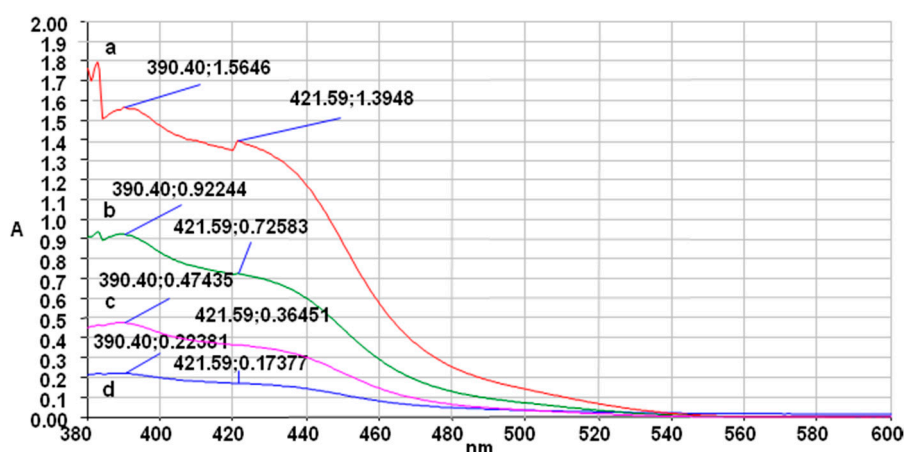


Figure 2. UV-Vis spectrum of compound **3** in CHCl_3 (Concentration a. $7.64 \times 10^{-5} \text{ mol L}^{-1}$; b. $3.82 \times 10^{-5} \text{ mol L}^{-1}$; c. $1.91 \times 10^{-5} \text{ mol L}^{-1}$; d. $7.64 \times 10^{-6} \text{ mol L}^{-1}$).

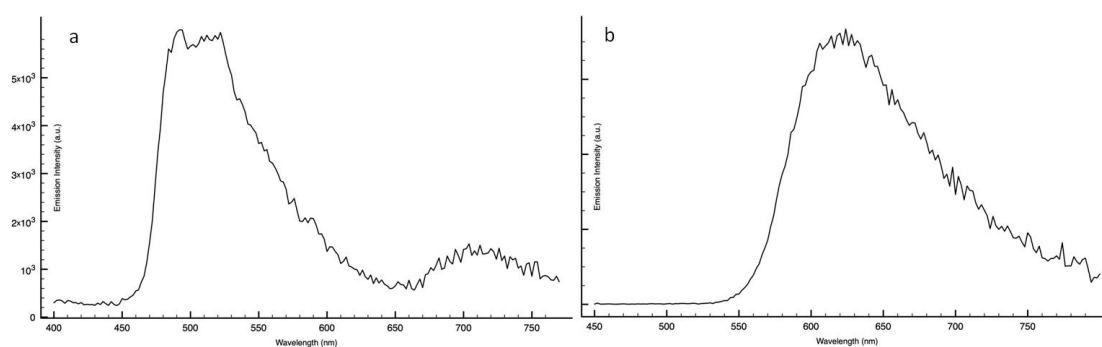


Figure 3. (a) Emission spectrum of compound **3** in CH_3CN (Concentration $3.47 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda_{\text{max}} = 508 \text{ nm}$); (b) Solid state emission spectrum of compound **3** ($\lambda_{\text{max}} 680 \text{ nm}$).

A similar compound, namely 1-(4-methoxyphenyl)-2-(2,4,6-trimethoxyphenyl)diazene **4** (Figure 4) has been reported [12] as red dye. The reported synthesis was made starting from 1,3,5-trimethoxyphenyl lithium and **2** in THF at $-78\text{ }^{\circ}\text{C}$ under inert atmosphere; to the best of our knowledge, no information about fluorescence of it has been reported. We synthesized compound **4** under the experimental conditions currently reported for the preparation of **3**, and no fluorescence was observed.

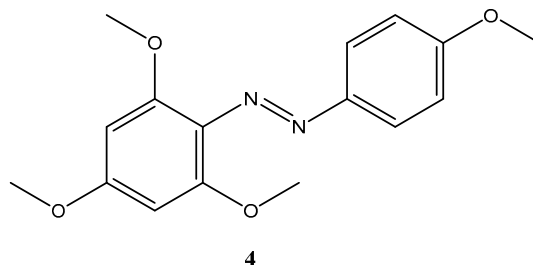


Figure 4. 1-(4-Methoxyphenyl)-2-(2,4,6-trimethoxyphenyl)diazene.

The only difference between compound **3** and **4** is the presence, in the latter, of a methoxy group instead of an hydroxy group. Probably, the presence of the hydroxy group in the *ortho* position with respect to the aza-group in compound **3** is able to block, through an intramolecular hydrogen bond, the isomerisation of the aza group, thus giving to the molecule fluorescent characteristics [9–11].

3. Materials and Methods

The ^1H -, ^{13}C NMR spectra were recorded on a Mercury 400 (Varian, Palo Alto, CA, USA) spectrometer operating at 400 MHz (for ^1H NMR), at 100.6 MHz (for ^{13}C NMR). Chemical shifts are referenced to the solvent for ^1H - and ^{13}C NMR (7.26 and 77.0 ppm, respectively for CDCl_3 and 2.50 and 39.50 ppm, respectively for $\text{DMSO}-d_6$). Signal multiplicities were established by DEPT experiments. Chemical shifts have been measured in δ (ppm). J values are given in Hertz. Electron spray ionization mass spectrum (ESI–MS) was recorded with a WATERS 2Q 4000 instrument (Waters, Etten-Leur, The Netherlands). IR spectrum was recorded using a Fourier transform spectrophotometer PerkinElmer (Waltham, MA, USA) FT-IR spectrometer Spectrum Two in the $4000\text{--}500\text{ cm}^{-1}$ wavelength range, using a NaCl cell. UV-Vis spectrum was recorded using a PerkinElmer (Waltham, MA, USA) UV-Vis spectrometer Lambda 12. Chromatographic purifications (FC) were carried out on glass columns packed with silica gel (Merck grade 9385, 230–400 mesh particle size, 60 \AA pore size) at medium pressure. Thin layer chromatography (TLC) was performed on silica gel 60 F254 coated aluminium foils (Fluka, Darmstadt, Germany). 3,5-Dimethoxyphenol and 4-methoxy benzenediazonium tetrafluoroborate were purchased by Sigma-Aldrich (Darmstadt, Germany).

Synthesis of 3,5-Dimethoxy-2-[(4-methoxyphenyl)diazenyl]phenol (**3**)

In a round bottom flask equipped with a condenser, under magnetic stirring, 3,5-dimethoxyphenol (0.200 mmol, 30.8 mg) and 4-methoxybenzenediazonium tetrafluoroborate (0.200 mmol, 44.4 mg) were added in 2 mL of acetonitrile. The reaction was heated to reflux. The reaction was monitored by TLC (eluent CH_2Cl_2). During the reaction, a precipitate was formed. After 12 h, the solid was collected by filtration. The mother liquor was concentrated under vacuum, and the product was purified by silica gel column chromatography (eluent CH_2Cl_2). The product obtained by filtration and that obtained by chromatography are combined to give 83% total yield.

Red plates m.p.: $209.1\text{--}209.8\text{ }^{\circ}\text{C}$ (MeCN); yield 48 mg, 83%; ^1H NMR (400 MHz, $\text{DMSO}-d_6$, $25\text{ }^{\circ}\text{C}$) δ ppm: 8.36 (d, $J = 9.0\text{ Hz}$, 2H), 7.95 (d, $J = 9.0\text{ Hz}$, 2H), 6.25 (s, 2H), 4.00 (s, 3H), 3.91 (s, 3H), 3.75 (s, 3H); ^{13}C NMR: (100.6 MHz, $\text{DMSO}-d_6$, $25\text{ }^{\circ}\text{C}$) δ ppm: 164.7 (C), 160.8 (C), 159.6 (C), 157.0 (C), 143.7 (C), 123.2 (C), 122.8 (CH), 114.8 (CH), 93.6 (CH), 91.5 (CH), 56.2 (CH_3), 55.8 (CH_3), 55.6 (CH_3); ^1H NMR (400 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$) δ ppm: 7.75 (d, $J = 9.0\text{ Hz}$, 2H), 6.97 (d, $J = 9.0\text{ Hz}$, 2H), 6.06 (d, $J = 2.3\text{ Hz}$,

1H), 6.03 (d, $J = 2.3$ Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H); ^{13}C NMR: (100.6 MHz, CDCl_3 , 25 °C) δ ppm: 165.1 (C), 160.8 (C), 159.7 (C), 159.4 (C), 143.7 (C), 124.2 (C), 122.8 (CH), 114.5 (CH), 93.8 (CH), 91.5 (CH), 56.3 (CH_3), 55.6 (CH_3), 55.5 (CH_3); ESI-MS (m/z): 289 ($\text{M} + \text{H}$)⁺, 311 ($\text{M} + \text{Na}$)⁺, 327 ($\text{M} + \text{K}$)⁺; FT-IR (cm^{-1}): 3686, 3614, 3020, 2400, 1605, 1525, 1421, 1223, 1211, 790, 725, 672, 515; UV-vis (CHCl_3) $\lambda_{\text{max}} = 390$ nm, $\epsilon_{390} = 21,445$ L mol⁻¹ cm⁻¹; Elemental analysis for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_4$ calculated C 62.49; H 5.59; N 9.72; O 22.20, found C 62.69; H 5.61; N 9.73.

Supplementary Materials: The following are available online, Figure S1. ^1H NMR spectrum of compound **3** in CDCl_3 ; Figure S2. ^{13}C NMR spectrum of compound **3** in CDCl_3 ; Figure S3. DEPT spectrum of compound **3** in CDCl_3 ; Figure S4. ^1H NMR spectrum of compound **3** in $\text{DMSO}-d_6$; Figure S5. ^{13}C NMR spectrum of compound **3** in $\text{DMSO}-d_6$; Figure S6. DEPT spectrum of compound **3** in $\text{DMSO}-d_6$; Figure S7. ESI-MS spectrum of compound **3**; Figure S8. FT-IR spectrum of compound **3**.

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Conflicts of Interest: The authors declare no conflict of interest.

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